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Disorder-induced temperature dependence of the radiative lifetime of Frenkel excitons in molecular aggregates

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Abstract

We calculate the temperature dependence of the fluorescence decay of a 1D localized Frenkel exciton resulting from the thermal redistribution of population over the localized states. The Pauli master equation is used to describe the exciton hopping.

Keywords: Frenkel excitons; Molecular aggregates; Exciton transport

1. Introduction

Nowadays it is well established that many spectroscopic features of linear molecular aggregates are governed by one-dimensional (1D) Frenkel exciton states. It was found in several experimental studies of *J*-aggregates of different types, e.g., pseudoisocyanine (PIC) [1], 1,1′-diethyl-3,3′-bis(sulfopropyl)-5,5′,6, 6′-tetrachlorobenzimidacarbocyanine (BIC) [2], 3,3′-bis (sulfopropyl)-5,5′ -dichloro-9-ethylthiacarbocyanine (THIATS) [3], that the exciton radiative lifetime went up with increasing the temperature. This slowing down of the aggregate radiative dynamics was attributed to the effect of thermal population of the higher exciton states, which have the oscillator strengths small compared to the typical oscillator strength of the optically dominant exciton states that occur at the exciton band bottom [1,4–6].

The goal of the present paper is to analyze the temperature dependence of the fluorescence decay time of localized 1D Frenkel excitons taking into account the following factors: (i) *localization* of the exciton states, (ii) coupling of localized excitons to the *host vibrations* (not only to the vibrations of the aggregate itself) [7,8], and a possible *non-equilibrium* of the subsystem of localized excitons on the time scale of the emission process. We use the Pauli master equation as a tool for the description of the vibration-assisted redistribution of Frenkel excitons over the localized states. The rates, entering this equation, are calculated as the overlap integrals of the squared localized

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exciton wave functions times the usual vibration occupation numbers, which account for the detailed balance principle [10]. This approach is applied to numerically simulate the temperature dependence of the exciton fluorescence decay time.

2. The model

We model an aggregate as $N(N \gg 1)$ optically active two-level molecules forming a regular 1D lattice. The corresponding Frenkel exciton Hamiltonian reads [9]

$$H_{\mathrm{ex}} = \sum_{n=1}^{N} \varepsilon_n |n\rangle\langle n| + \sum_{n,\,m}^{N} J_{nm} |n\rangle\langle m|. \tag{1}$$

Here $|n\rangle$ is the state vector of the excited nth molecule with the energy ε_n. The energies ε_n are assumed to be uncorrelated (for different sites) Gaussian stochastic variables with zero mean and the standard deviation σ. The inter-site interactions J_{nm} are considered to be non-fluctuating. We will not restrict ourselves to nearest-neighbor approximation, but account for general dipole–dipole interactions: $J_{nm} = J/|n-m|^3, (J_{nn} \equiv 0)$. Here J is the nearest-neighbor coupling. For J-aggregates, J is negative and the states coupled to the light are those at the bottom of the exciton band. The ratio $\sigma/|J|$ will be referred to as the disorder degree.

At the relatively small magnitude of the disorder degree $\sigma/|J|$ that we will be dealing with, a convenient basis of the wave functions to analyze the problem is that which diagonalizes the Frenkel Hamiltonian (1)

$$|v\rangle = \sum_{n=1}^{N} \varphi_{vn} |n\rangle, \quad \sum_{m=1}^{N} H_{\mathrm{ex}}^{nm} \varphi_{vm} = E_v \varphi_{vn}, \tag{2}$$

where $H_{\mathrm{ex}}^{nm} = \langle n|H_{\mathrm{ex}}|m\rangle$, φ_{vn} is the exciton eigenfunction in the site representation corresponding to the eigenvalue E_v, and v ranges from 1 to N.

Coupling of the excitons to vibrations leads to transfer of population between the localized exciton states. For a relatively weak linear on-site exciton–host vibration coupling, the hopping rate from state v' to v can be calculated using first-order perturbation theory [10,11] and is given by

$$W_{vv'} = W_0 S(|\varepsilon_{vv'}|) \sum_{n=1}^{N} \varphi_{vn}^2 \varphi_{nv'}^2 \{\Theta(\varepsilon_{vv'}) n(\varepsilon_{vv'}) + \Theta(-\varepsilon_{vv'})[n(-\varepsilon_{vv'}) + 1]\}. \tag{3}$$

Here, $n(\varepsilon_{vv'}) = \left[\exp\left(\varepsilon_{vv'}/k_{\mathrm{B}}T\right) - 1\right]^{-1}$ is the mean occupation number of a normal vibration mode with the energy $\varepsilon_{vv'} = E_v - E_{v'}$, k_{B} is the Boltzmann constant, and $\Theta(x) = 1(0)$ if $x > 0$ $(x < 0)$. The spectral function $S(\varepsilon_{vv'})$ depends on the model of the exciton–host vibration interaction. We set hereafter $S(\varepsilon_{vv'}) = |E_v - E_{v'}|/|J|$ to account for the long-wavelength acoustic limit [9]. The hopping rates given by Eq. (3) obey the principle of detailed balance, $W_{vv'} = W_{v'v}\exp\left[(E_{v'} - E_v)/k_{\mathrm{B}}T\right]$, which guarantees that eventually the excitons arrive at the proper equilibrium state characterized by the Boltzmann distribution over energy.

In order to describe the kinetics of hopping and emission processes, we employ the master equation for the populations of the localized exciton states, $P_v(t)$:

$$\dot{P}_v = -\gamma_v P_v + \sum_{v'=1}^{N} (W_{vv'} P_{v'} - W_{v'v} P_v), \tag{4}$$

where the dot denotes the time derivative and $\gamma_v = \gamma_0 \left(\sum_{n=1}^{N} \varphi_{vn}\right)^2$ is the spontaneous emission rate of the vth excitonic state, γ_0 being the spontaneous emission rate of a monomer. The fluorescence decay time τ is calculated as the integrated kinetics of the total population $P(t) = \sum_{v=1}^{N} P_v(t)$:

$$\tau = \int_0^{\infty} \mathrm{d}t \langle P(t)\rangle, \tag{5}$$

where the brackets denote the average over the energy disorder (ε_n).

3. Results of numerical simulations

Numerical simulations were performed for a chain of length $N = 500$. We calculated the exciton eigenfunctions φ_{vn} and eigenenergies E_v by diagonalizing numerically the Frenkel Hamiltonian (1) for a particular realization of the

disorder. The initial population was created within a window $-2.325|J|<E<-2.275|J|$ at the blue wing of the absorption spectrum, similar to the conditions of the experiments reported in Refs. [1–3]. The absorption and time-dependent fluorescence spectra were calculated as follows:

$$A(E)=\frac{1}{N}\left\langle\sum_{v=1}^{N}\left(\sum_{n=1}^{N}\varphi_{vn}\right)^{2}\delta(E-E_v)\right\rangle, \tag{6}$$

$$I(E,t)=\frac{1}{N}\left\langle\sum_{v=1}^{N}\gamma_v P_v(t)\delta(E-E_v)\right\rangle, \tag{7}$$

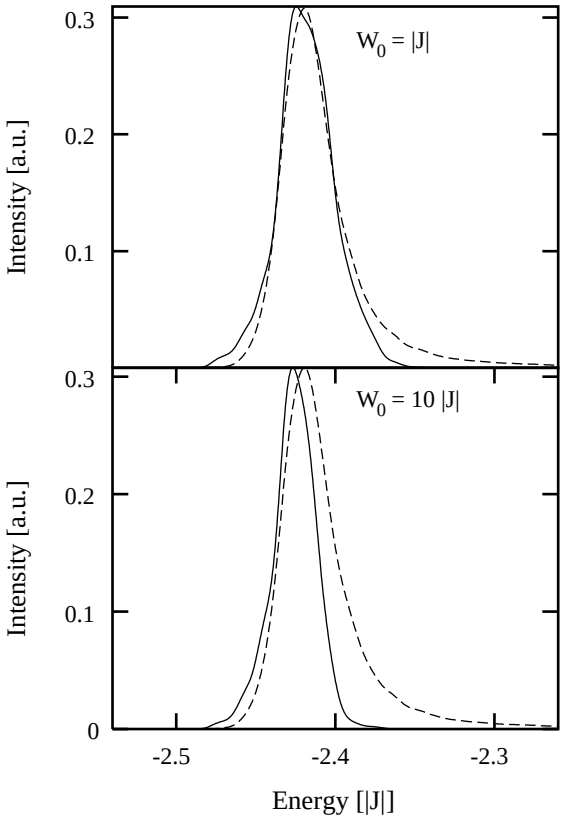

Fig. 1. Exciton optical spectra obtained by numerical simulations of a disordered chain of length $N=500$ at the disorder degree $\sigma=0.1|J|$. The dashed and solid lines present the absorption band and the zero-temperature fluorescence spectra, respectively, in the limits of slow ($W_0=|J|$, upper panel) and fast ($W_0=10|J|$, lower panel) vibration-assisted hopping. The presented spectra have been collected at the instant of time where the population has decayed to 0.2 of its initial value.

using the smoothing method described in Ref. [12]. The resulting kinetics was obtained by averaging over 50 realizations of the disorder.

Figs. 1 and 2 show the results of numerical simulations carried out for $\sigma=0.1|J|$ and $\gamma_0=2\times10^{-5}|J|$, which are parameters typical for PIC. In Fig. 1, we depicted the absorption spectrum (the solid line) as well as the zero-temperature fluorescence spectra obtained for two values of the exciton hopping parameter: $W_0=|J|$ and $W_0=10|J|$ (the dashed lines). As is seen, at $W_0=|J|$ the fluorescence spectrum nearly coincides with the absorption band, while at $W_0=10|J|$ it manifests a well-pronounced red shift. It is to be noted that similar features are characteristic for the experimentally observed fluorescence spectra in PIC [1] and BIC [2] J-aggregates, respectively. We refer to these two different limits as to the slow (no red shift) and fast (a visible red shift) vibration-assisted exciton hopping. The terms "slow" and

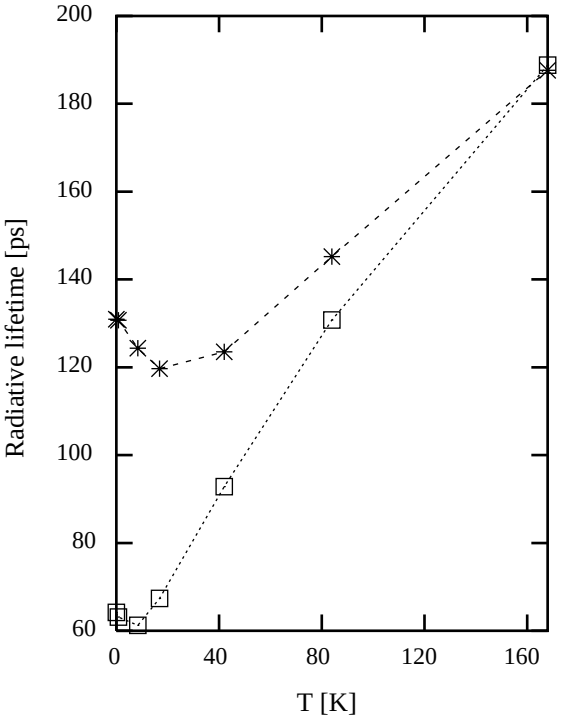

Fig. 2. Temperature dependence of the fluorescence decay time calculated for the same conditions as in Fig. 1. The dashed and dotted curve correspond to the exciton hopping parameter $W_0=|J|$ and $W_0=10|J|$, respectively.

"fast" are related to the exciton radiative decay scale. The typical radiative rate of the optically dominant exciton states equals $\gamma = \gamma_0 N^*$, where $N^* \approx 50$ for the disorder degree $\sigma = 0.1|J|$ [13]. Thus, $\gamma \approx 50\,\gamma_0 = 10^{-3}|J|$. Rescaling γ to dimensional units, using $|J| = 1.8\times10^{13}\,\mathrm{s}^{-1}$ $(600\,\mathrm{cm}^{-1})$, gives us $\gamma = 1.8\times10^{10}\,\mathrm{s}^{-1}$. This should be compared with the typical down-hill exciton hopping rate W_{12} for two consecutive states localized within the same localization segment. Using the estimates $\sum_n \varphi_{1n}^2\varphi_{2n}^2 \approx 1/N^* \approx 0.02$ and $E_2 - E_1 \approx \sigma/\sqrt{N^*} \approx 0.014|J|$ [4], one gets $W_{12} \approx 0.0003\,W_0$. Thus, W_{12} is approximately three times smaller or larger than γ for $W_0 = |J|$ and $W_0 = 10|J|$, respectively.

Fig. 2 presents the temperature dependence of the fluorescence decay time calculated according to Eq. (5) in the limits of a slow ($W_0 = |J|$) and a fast ($W_0 = 10|J|$) vibration-assisted hopping. We see drastic differences in the behavior for these two cases. At slow vibration-assisted hopping, the curve first even goes down upon increasing the temperature, reaches a minimum and then goes up. We stress that it starts from a value $\tau(0) \approx 130$ ps which is more than twice as large as $\gamma^{-1} = 55$ ps, and reflects in fact the rate of the exciton relaxation W_{12} from the non-radiating state (2) to the radiating state (1). More generally, at slow vibration-assisted hopping, the fluorescence decay is determined by the vibration relaxation to the optically dominant states.

At fast exciton hopping, we have $\tau(0) \approx 60$ ps, which is in fact the exciton radiative lifetime at zero temperature. Further, τ increases upon heating. Here, after excitation, the excitons rapidly relax after the excitation event to the radiating states, and the fluorescence decay is determined by the exciton spontaneous emission.

4. Summary

In this paper, we studied the temperature dependence of the fluorescence decay time of 1D localized Frenkel excitons resulting from the vibration-assisted redistribution of excitons over the localized states. On the basis of our numerical simulations, we conclude that measuring the fluorescence decay only gives adequate information about the exciton radiative lifetime if the vibration-assisted exciton hopping is fast compared to the radiative dynamics. In the opposite limit, the fluorescence decay reflects the rate of the exciton intra-band relaxation rather than the exciton radiative rate.

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